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I, DAVID DANIEL CLARKE, ASSISTANT DIRECTOR PATENT SERVICES, hereby certify that the annexed are true copies of the Provisional specification and drawing(s) as filed on 15 November 1993 in connection with Application No. PM 2432 for a patent by APECS INVESTMENT CASTINGS PTY LTD filed on 15 November 1993.

I further certify that the annexed documents are not, as yet, open to public inspection.

WITNESS my hand this Fourth day of July 1994.

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DELEGATE OF COMMISSIONER OF PATENTS

SILVER ALLOY COMPOSITIONS

This invention relates to silver alloy compositions.

This invention has particular reference to silver alloy compositions for jewellery, coinage and other applications where a work hardening alloy is required and for illustrative purposes reference will be made to this application. However, it is to be understood that this invention could be used to produce other types of silver alloys suitable for use as for example, electrical contacts or the like.

In general, silver as a material for the production of silver jewellery, certain coinage and the like is specified to comprise at least 925 parts per thousand by weight fine silver and is specified as ".925 silver". .925 silver accordingly typically comprises an alloy 92.5% by weight silver, generally alloyed with copper for hardness traces of other metals as additives or impurities.

Conventional silver alloys of the .925 type have several disadvantages in a manufacturing jewellery and other materials engineering contexts. Principal limitations include difficulties in providing suitable work hardening characteristics and a characteristic firescale formation tendency attributable to oxidation of copper and other metals at the surface of cast or hot worked pieces.

Several formulations have been proposed to overcome one or the other of the aforementioned disadvantages. United States Patent Nos. 5039479 and 4973446 disclose alloys of silver and master alloys for the production of such silver

alloys having superior qualities over conventional alloys, and including, in addition to silver, controlled amounts of copper and zinc, together with tin, indium, boron and silicon. The compositions exhibit reduced porosity, grain size and fire scale production, and have acquired wide utilisation in silver jewellery production. It is presumed but not established that the addition of zinc to such compositions provides at least a degree of antioxidant properties to the compositions when hot worked and improves colour, thus limiting the formation of principally copper oxide based fire scale, and reducing silver and copper oxide formation resulting in formation of pores in the cast or recast alloys. Silicon appears also to function as an antioxidant, thereby reducing firescale formation.

A disadvantage of the hereinbefore described firescale resisting alloys is that the alloys exhibit poor work hardening qualities thus not achieving the mechanical strength of traditional worked .925 silver goods.

The present invention aims to substantially alleviate at least one of the above disadvantages and to provide silver alloy compositions which will be reliable and efficient in use. Other objects and advantages of this invention will hereinafter become apparent.

With the foregoing and other objects in view, this invention in one aspect resides broadly in silver alloy compositions including:-

80 - 99.0% by weight silver;

0.5 - 6% by weight copper;

0.02 - 7% by weight of a firescale resisting additive selected from one or a mixture of zinc and silicon, and

0.01 - 2.5% by weight germanium.

The silver content of the alloy may be selected to be in the amounts commonly specified for grading silver. For example, the alloy may comprise from 89 to 95% by weight silver. Preferably, the alloy contains a proportion of silver required for .925 silver, that is at least 92.5% by weight. The copper content of the alloy may be selected according to the hardness required of the cast alloy. For example, for manufacturing jewellers .925 alloy, the copper content may advantageously be in the range of from 2.0 to 3.0 % by weight.

The zinc content of the alloy has a bearing on the colour of the alloy as well as functioning as a reducing agent for silver and copper oxides. Preferably, the amount of zinc used is selected to be between 2.0 and 4.0% by weight. The silicon content of the alloy is preferably adjusted relative to the proportion of zinc used to provide the desired firescale resistance whilst maintaining a suitable colour commensurate with the zinc content of the alloy, and may for example advantageously fall within the range of 0.15 to 0.2% by weight.

The germanium content of the alloy has surprisingly resulted in alloys having work hardening characteristics of a kind with those exhibited by conventional .925 silver alloys,

together with the firescale resistance of the hereinbefore described firescale resistant alloys. In general, it has been determined that amounts of germanium in the alloy of from 0.4 to 2.0% by weight provide a work hardening modifying result on alloys of the firescale resistant kind not including germanium. However, it is noted that the hardening performance is not linear with increasing germanium nor is the hardening linear with degree of work.

Preferably, the alloy also includes rheology modifying and other additives to aid in improving the castability and/or wetting performance of the molten alloy. For example, 0.0 - 3.5% by weight of a modifying additive selected from one or a mixture of indium and boron may be advantageously added to the alloy to provide grain refinement and/or reduce surface tension, thereby providing greater wettability of the molten alloy.

Accordingly, in a further aspect, this invention resides in silver alloy compositions including:-

89 - 95% by weight silver;
0.5 - 6% by weight copper;
0.05 - 5% by weight zinc;
0.02 - 2% by weight silicon;
0.001 - 2% by weight boron;
0.01 - 1.5% by weight indium, and
0.01 - 2.5% by weight germanium.

In order that this invention may be more readily understood and put into practical effect, reference will now

be made to the following example which describes a preferred embodiment of the invention.

Example 1

An alloy consisting of the following constituents (by weight) and being in accordance with United States patent No. 5039479 was provided as a first control:

silver	92.5%
copper	3.29%
zinc	3.75%
indium	0.25%
boron	0.01%
silicon	0.2%

This alloy is known as and will be referred to hereinafter as "UPM alloy". As a second control, a commercial sterling silver was used, comprising 92.5 % by weight silver and the balance mainly copper.

Samples of the controls were cast and the hardness of each were measured as cast, at 50% and 75% work and annealed, according to the Vickers hardness VH scale. As used hereinafter the terms "50% work" and "75% work" mean subjecting a cast sample to cold rolling to 50% and 25% of its original thickness respectively.

Three alloys A to C in accordance with the present invention were prepared to the following compositions:

	ALLOY A	ALLOY B	ALLOY C
Ag	92.5	92.5	92.5
Cu	2.35	3.25	3.0

Zn	2.82	3.75	3.14
Si	0.19	0.2	0.15
B	0.01	0.01	0.01
In	0.23	0.25	0.2
Ge	1.9	0.04	1.0

The three alloys were cast into samples as per the controls and were tested for Vickers Hardness as cast, at 50% and 75% work and annealed. The hardness results for the controls and alloys A, B, and C are as follows:

ALLOY	VH AS CAST	VH @ 50% WORK	VH @75% WORK	VH ANNEALED
STERLING	75.4	133	150	59
UPM	67	135	153	58.3
A	70.2	146	150	59.6
B	72.4	135	143	61.3
C	77.2	123	159	63.6

It can be seen that the alloy B having only 0.04% by weight Ge is harder than UPM and softer than sterling when cast, but that all three alloys are on par at 50% work. Alloy B exhibited a softening relative to the controls at 75% work and is hardest relative to the controls when annealed. Alloy C, having 1.0% by weight Ge, exhibits an as-cast hardness on par with sterling, is softer than UPM or sterling at 50% work, but is markedly harder than these two alloys at 75% work. Alloy A, having 1.9% by weight Ge, exhibits as-cast hardness between that of UPM and sterling, is markedly harder than these two alloys at 50% work, but does not increase hardness as much as the controls upon further work to 75%.

In use, alloys in accordance with the above embodiments and in accordance with the present invention may be selected by tailoring the germanium content of the alloys to provide the desired work hardening characteristics. The non-linear effect of use of germanium and the ability to vary other elements such as copper provides for production of a range of firescale resistant alloys of selected work hardenability.

It will of course be realised that while the above has been given by way of illustrative example of this invention, all such and other modifications and variations thereto as would be apparent to persons skilled in the art are deemed to

fall within the broad scope and ambit of this invention as is herein set forth.

DATED THIS Fifteenth DAY OF November, 1993.

APECS INVESTMENTS PTY. LTD.

by

PIZZEY AND COMPANY PATENT ATTORNEYS